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XRD, phase transition and piezoelectric properties of La doped PBN ceramics

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Abstract : The lanthanum doped Lead Barium Niobate (PBN) ceramics were synthesized and characterized by the conventional ceramic techniques Structural parameters were discussed with respect to the doping ions The transition temperature and the grain size decreases with the lanthanum concentration Mechanical quality factor, charge coefficient and planar coupling constant were improved Maximum lattice anisotropy was observed in higher lanthanum containing compound

Keywords : Lead Barium Niobate (PBN) ceramics, piezoelectric properties, La dopants

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1. Introduction

Tungsten bronze ferroelectric materials are found to be technologically important materials for device applications due to their high dielectric constant (ε), piezoelectric and electrooptic properties. The search for these properties in this family, has stimulated much interest in a number of potential Morphotropic Phase Boundary (MPB) systems. This phase boundary generally occurs at nearly constant composition over a wide temperature range. The best known MPB system is lead barium niobate (PBN, $Pb_{1-x}Ba_xNb_2O_6$). The piezoelectric properties of lead metaniobate, $PbNb_2O_6$ was first reported by Goodman [1] with a high Curie temperature of 570°C and the resonant frequency is quite stable under varying temperatures. For device applications, ferroelectric ceramic compositions near the MPB are more suitable because induced piezoelectric effects are enhanced [2]. In addition

to the sintered ceramics, PBN has also been developed in the form of hot pressed, grain oriented ceramics [3,4] and bulk single crystals [5,6]. Hence, the authors have investigated the effect of lanthanum (La^{3+}) on various physical and electrical properties of PBN ceramics.

2. Experimental

The ceramics are prepared with the following compositions.

(1) $Pb_{0.75}Ba_{0.1}K_{0.30}Nb_2O_6$, (2) $Pb_{0.70}Ba_{0.1}K_{0.25}La_{0.05}Nb_2O_6$,

(2) $Pb_{0.70}Ba_{0.1}K_{0.10}La_{0.10}Nb_2O_6$, (4) $Pb_{0.625}Ba_{0.1}K_{0.10}La_{0.15}Nb_2O_6$.

Pure compound (source [7]) is $Pb_{0.60}Ba_{0.40}Nb_2O_6$.

Processing of ceramic compacts :

Preparation of dense ceramics and polling of PBN ceramics is somewhat difficult compared to other ferroelectric composition. Under certain conditions, partial substitution of Pb^{2+} or Nb^{5+} with other similar ions, has been one of the advantages of improving the sinterability and ceramic properties [8,9]. The starting materials are A.R. grade oxides/carbonates of 99.99% purity.

Calcination :

The powder was heated to above 2/3 of its melting point for several hours. After wet mixing, the slurry was dried in an oven. The dried mixture was heated in air at 900°C for 3 hours maintaining approximately 200°C/hr. Calcination is a crucial step [10] for removing unwanted gases and to effect thermochemical reactions.

Ceramic forming and shape :

The conventional ceramic method of cold pressing in a die punch assembly using a hydraulic press was adopted to compress into disc shape. To ensure good flow of the powder and reproducing filling of the die, the powder was seived and granulated using 5% PVA and a pressure of 3–4 tons/inch^2 [2].

Sintering :

The die pressed discs were placed on a platinum foil and covered the discs with a crucible to avoid Pb loss and heated in air for a sintering period of 2–5 hrs at 1290–1300°C to prepare different ceramic composition. Then the disc type samples were coated with air drying silver paste and fixed at 600°C for 1 hr to ensure good electrical contact on both sides.

Polling :

The polling for the above samples was performed in oil bath at 140°C by applying 20 KV/cm field for 1 hr. Then the specimens were field cooled to room temperature and

washed in benzene. The electrical measurements were carried on polled samples after 48 hrs after polling according to Indian Rare Earths (IRE) standards [11].

Characterization :

The physical densities of the sintered discs were measured by the usual liquid displacement method. Piezoelectric coupling coefficients were measured by the resonance-antiresonance technique [12] by using HPLF Impedance analyser model 4192 A. The charge coefficient, d_{33} was measured by using Berlin Court d_{33} meter. The sintered discs were ground into fine powder and subjected to X-ray diffraction for the analysis of crystal symmetry.

3. Results and discussion

X-ray diffraction studies :

The XRD patterns are given in Figure 1 from which the d spacings and lattice parameters (in Å) were calculated. The d spacings and peak intensities were compared with the values

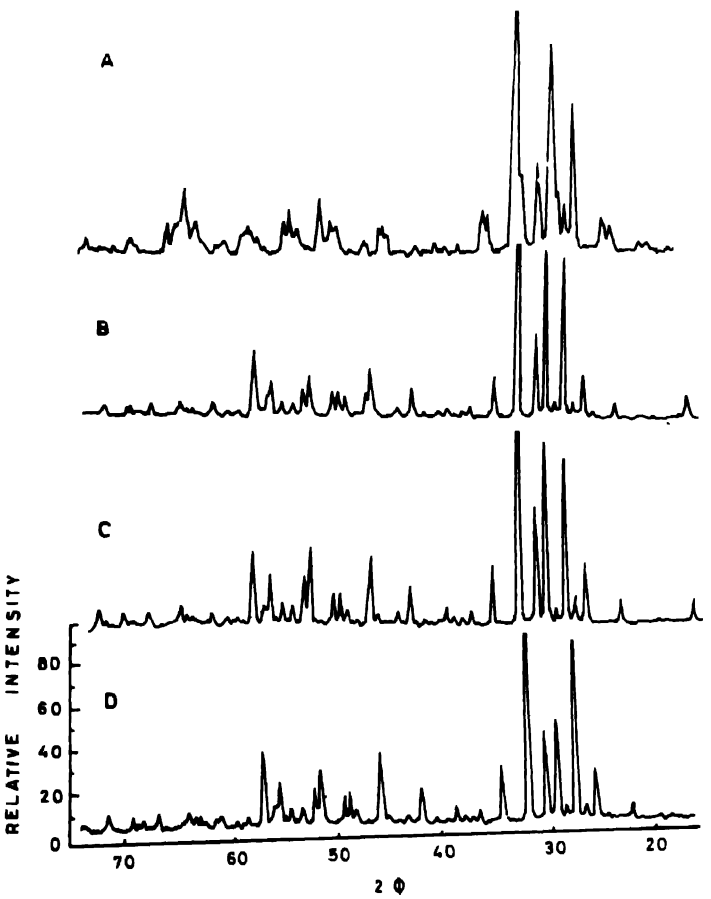

Figure 1. X-ray diffraction patterns of

(A) $Pb_{0.75}Ba_{0.1}K_{0.30}Nb_2O_6$, (B) $Pb_{0.70}Ba_{0.1}K_{0.25}La_{0.05}Nb_2O_6$,

(C) $Pb_{0.70}Ba_{0.1}K_{0.10}La_{0.10}Nb_2O_6$, (D) $Pb_{0.625}Ba_{0.1}K_{0.10}La_{0.15}Nb_2O_6$.

of $Pb_{0.70}Ba_{0.30}Nb_2O_6$ [13]. The XRD analysis confirmed orthorhombic symmetry in unmodified and modified PBN ceramics and the values are given in Table 1.

Table 1. Structural parameters of undoped and La doped PBN ceramics.

	a (Å)	*b* (Å)	*c* (Å)	$\sqrt{10}c/a$	Grain size μm
Pure	17.703	18.166	7.760	1.386	2 090
1	17.721	17.792	7.791	1.390	2.941
2	17.950	17.755	7.826	1.379	2 857
3	17.822	17.524	7.853	1.393	2 688
4	17.853	17.243	7 867	1.392	1.950

Density :

Theoretical densities were calculated from the volume of the unit cell dimensions obtained from the XRD using an equation given in our earlier paper [14]. They were compared with the experimental values. The measured densities are about 90–95% of the theoretical densities.

Scanning electron microscopy :

The scanning electron micrographs on fractured surfaces of the above samples have been shown in Figure 2 which inidcate that some of the grains are needle shaped (Figures 2A and C) and some are rounded. The average grain diameter was measured by linear intercept method [15,16] and have been given in Table 1. The average grain diameter appears to reduce with increasing dopant concentration which may be explained by the grain boundary mobility. The doped ions concentrate around the grain boundaries and reduce the mobility of grains there by decreasing the grain size. This reducing grain boundary mechanism was studied theoretically and experimentally by Jorgensen [17,18].

Also the percentage of porosity decreased with increasing the doping ion concentration as reflected by an improvement in the density. The sintering and grain growth behaviour of lead based ceramics are sensitive to certain additives like Ag, Nb, K, Ca and rare earth cations which accelerate the process of densification. The mechanism of densification can be explained as follows.

The process of densification takes place by liquid phase sintering in Pb based compounds [14]. Tungsten bronze structure has inherently some cation vacancies and doping ion increases the concentration of these vacancies. Due to the liquid phase and increased vacancies, rate of diffusion increases [19]; hence the doped rare-earth ions' mobility is increased to occupy the vacanies. Since the atomic weights of rare-earths are more than that of lead, the density of materials increases.

Plate I(a)

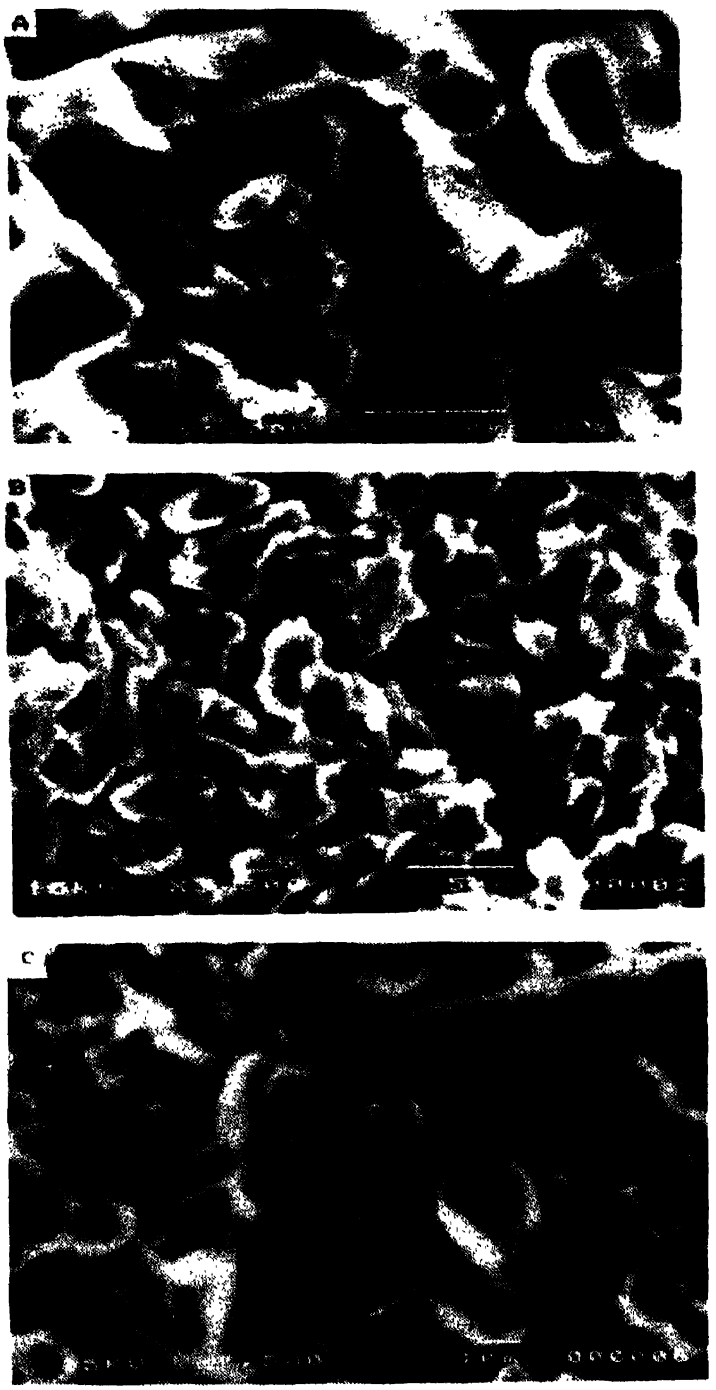

Figure 2. Scanning electron micrographs of (A) $Pb_{0.60}Ba_{0.40}Nb_2O_6$

Plate I(b)

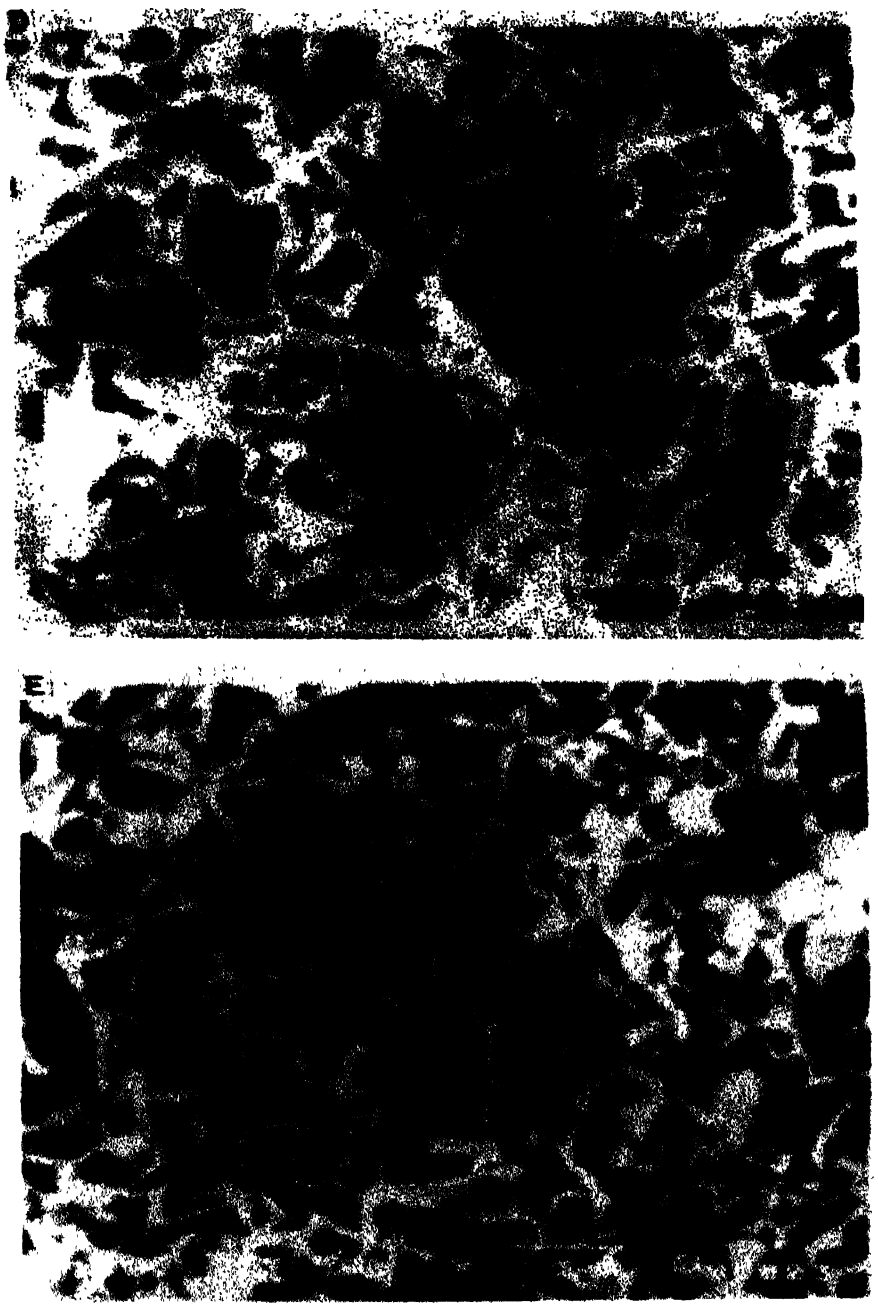

Figure 2. Scanning electron micrographs of (D) $Pb_{0.70}Ba_{0.1}K_{0.10}La_{0.10}Nb_2O_6$ and (E) $Pb_{0.625}Ba_{0.1}K_{0.10}La_{0.15}Nb_2O_6$.

Dielectric measurements :

The temperature variation of the dielectric constant was measured up to 450°C by using HP Impedance analyser model 4192 A and the graph is shown in Figure 3. The dielectric

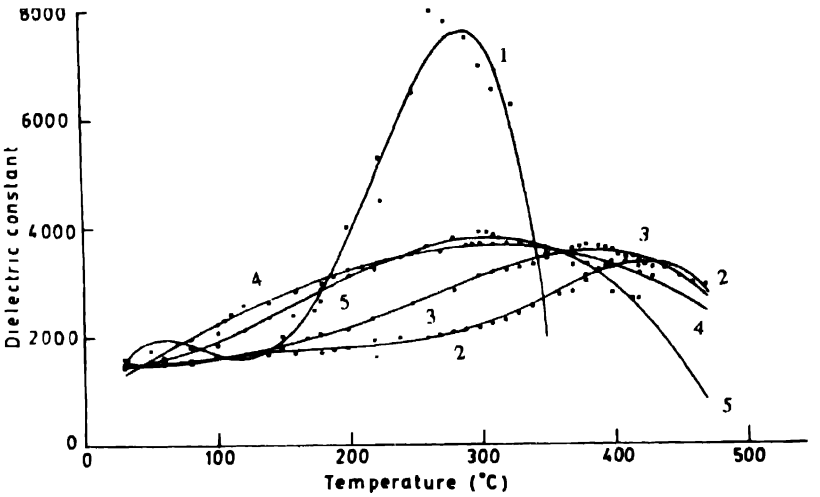

Figure 3. Dielectric constant as a function of temperature :
(1) $Pb_{0.60}Ba_{0.40}Nb_2O_6$, (2) $Pb_{0.75}Ba_{0.1}K_{0.30}Nb_2O_6$,
(3) $Pb_{0.70}Ba_{0.1}K_{0.25}La_{0.05}Nb_2O_6$, (4) $Pb_{0.70}Ba_{0.1}K_{0.10}La_{0.10}Nb_2O_6$,
(5) $Pb_{0.625}Ba_{0.1}K_{0.10}La_{0.15}Nb_2O_6$.

constant at room temperature (ε_{RT}) and at maximum temperature (ε_{max}) and transition temperature T_c shown in Table 2 indicate that the T_c value is increased from 265 to 415°C by introducing K^+ into the structure. Further, the T_c value is reduced to 305°C by adding La^{3+}. This trend was also observed in many tungsten bronze materials [20,21]. When rare-earths are introduced into the structure, the transition temperature will be decreased. The maximum dielectric constant was observed both at room temperature and at maximum temperature for pure compound when compared with the doped compounds.

Table 2. Dielectric and piezoelectric constants of undoped and La doped PBN ceramics.

Sample No	ρ	ε_{RT}	ε_{max}	T_c°C	tan δ	K_p%	Q_m	d_{33}
Pure	5 49	1600	7980	265	0.05	30	84	92
1	5.50	1466	3484	415	0.09	9.8	105	105
2	5.56	1450	3678	380	0.07	13	110	112
3	5.58	1438	3708	330	0.07	17	122	118
4	5.59	1440	3925	305	0.10	20	135	126

From Figure 3, it is very clear that the rise in dielectric constant with temperature is more predominant in undoped compounds than in other systems [22]; this is probably due

to the influence of rare-earth ions on the polarization state of the materials as a whole. The maximum dielectric constant at peak temperature for undoped compound is 7980 and this value decreased rapidly beyond the transition temperature whereas in other compounds, the rapid decrease in dielectric constant is not observed. Moreover, the maximum dielectric constant value spans over a wide temperature range with respect to the addition of La concentration. The area of dielectric peak is more predominant in higher La concentration (0.15). Similar results can also be observed in other rare earth dopants. The broadening increases with La concentration implying stabilization.

According to a theoretical model proposed by Dvor. and Glokar [23], the presence of La^{3+} changes the harmonic forces and the planar frequencies of the ferroelectric phase at the transition. The decrease in T_C as well as dielectric constant value in PBN system implies that the substitution cation (La^{3+}) in A site may reduce the dipole moment and lowers the value of ε_{Tc}. The similar trend was observed in other niobates [24]. The decrease in maximum dielectric constant and ferroelectric-paraelectric shift to lower side in the materials under investigation can also be explained on the basis of domain wall formation, space-charge effects and dielectric broadening model [25]. Also the lowering of ε_{max} value may be attributed to the fluctuation in the composition.

Piezoelectric properties and significance of various constants :

Elastic bodies exhibit numerous resonances on excitation. The most pronounced are those where the body can just accommodate one half wavelength of a standing elastic wave. In poled ceramics, such elastic waves can be excited and the interaction of mechanical resonance with electrical behaviour can be observed. If a piezoelectric crystal is considered equivalent to an LCR circuit, impedance will be low at resonance. The frequency of minimum impedance is called resonance frequency (f_r) and the frequency of maximum impedance is called antiresonance frequency (f_a).

Piezoelectric properties of various practical devices using the piezoelectric effect has been the subject of many researchers. The selection of materials for device applications, depends on the properties of piezo ceramics. The basis for evaluating the piezoelectric properties of a ferroelectric ceramic is its electromechanical coupling coefficient or planar coupling constant (K_p) and its mechanical quality factor (Q_m). Further, the two transverse or piezoelectric strain coefficients (charge coefficient d_{31} and voltage coefficient g_{31}) are important parameters to be considered for this purpose. The K_p determines the percentage of the total input electrical energy stored in mechanical form.

Any ceramic to be used as a wave filter should have high room temperature dielectric constant (ε_{RT}), high K_p and high Q_m. For electric wave applications, the ceramic material should provide an optimum K_p value which is to be selected from a wide range extending from an extremely large to a very small value. The planar coupling constant determines the frequency spacing between the attenuation poles of the filter in such a manner that a ceramic with greater K_p value produces a wider spacing and a narrow frequency spacing with low K_p can be obtained in the wave filter [26,27].

The behaviour of the above constants depends upon the doping ion concentration at room temperature. The K_p value was found to be 9.8% when PBN was doped with potassium and doping the La^{3+} and increasing its concentration increased this value to 20% (Table 2). So it is clear that the addition of La hardens the material and improves the coupling constant.

The Q_m determines the loss in the pass band and the loss in the attenuation poles in the filter. Therefore for low loss which is desired in wave filters, a ceramic with high Q_m value is desired. The ceramics studied in this paper, have high ϵ_{RT} and K_p compared to doped $PbTiO_3$ ceramics [14,28] and are quite suitable for application in ceramic electric wave filters. The charge coefficient d_{33} was found to increase with increasing La concentration and the values are well matched with literature values [29].

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